Iron(III) complexes with naturally occurring organic ligands in seawater

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Introduction

Iron is a very important micronutient of the primary production process in seawater, especially in „HNLC“ (High Nutrient Low Chlorophyll) areas in the oceans, where the primary production is insufficiently expressed (despite sufficient macronutrient concentrations) because of the bioavailable iron deficiency.[1-3] According to the „iron hypothesis“, the stimulation of primary production process, as a result of natural or artificial iron enrichment, then could contribute to the drawdown of atmospheric CO_2 by increasing the efficiency of the biological pump (Fig.1).[2-4] The „iron hypothesis“ was confirmed in numerous mezoscale artificial enrichment experiments,[3] although their effect wasn't longlasting since they used acidified aqueous solution of iron(II). Therefore, important question is in which form iron should be added in seawater in order to keep it dissolved for a sufficient period of time to be available to photosynthetic organisms. Citric, malic and succinic acid are naturally occurring ligands that could form complexes with Fe(III) that will be bioavailable to organisms.

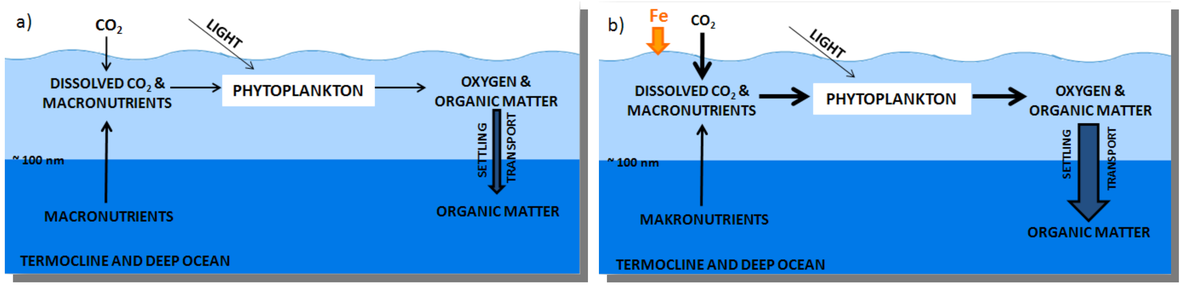

Figure 1. The iron hypothesis. a) The efficiency of the biological pump under normal conditions. b) Efficiency of the biological pump as a result of Fe enrichment.[2]

Results and discussion

Measurements were preformed in model aqueous solutions (0.55 mol dm^{-3} NaCl and 0.7 mol dm^{-3} $NaClO_4$) using square-wave (SW) voltammetry (a = 25 mV; f = 50 s^{-1}; step increment = 2 mV) and UV-Vis spectrophotometry.

I. Fe(III)-succinate complexes

Two different redox processes (Fig. 2) in pH range from 5.2 to 7.4 were registered: with c_{suc} = 0.04-0.12 mol dm^{-3}, Fe(III)-succinate reduction process 1 and with c_{suc} = 0.12-0.3 mol dm^{-3} Fe(III)-succinate process 2. Voltammetric measurements indicated that process 1 corresponds to reduction of complex with ratio Fe(III):succinate = 1:2.
The formation kinetics of both complexes was slow, Fe(III)-succinate complex 1 was equilibrated within 17 h, and Fe(III)-succinate complex 2 in about 10 h. However, after equilibration period, complex 1 was stable in the solution for about a week, and complex 2 for about 10 h.
The UV-Vis spectra (Fig. 3) analysis presumed that stoichiometry ratio of Fe(III):succinate complexes 1 and 2 was 1:2 and 1:3, respectively.

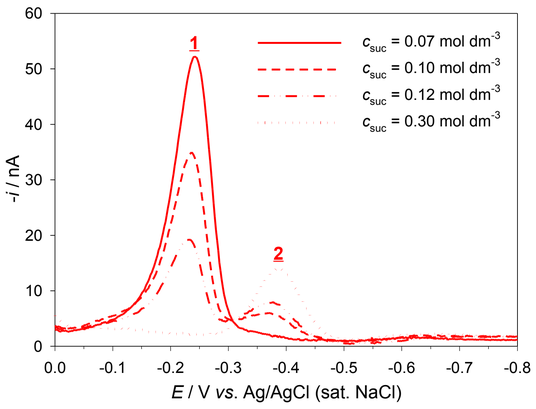

Figure 2. Voltamograms of Fe(III)-succinate complexes at different c_{suc}. pH = 6.0, c_{Fe} = 4 x10^{-5} mol dm^{-3}, t_{eq} = 17 h.

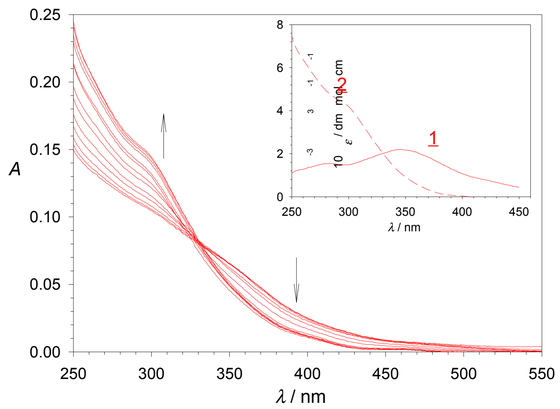

Figure 3. UV-Vis spectra of Fe(III)-succinate complexes recorded as function of c_{suc}. pH= 6.0, t_{eq}= 17 h c_{suc} = 0.04-0.3 mol dm^{-3}, c_{Fe} = 4x10^{-5} mol dm^{-3}, l = 1 cm. Inset: calculated electronic spectra.

II. Fe(III)-malate complexes

Three different redox processes (Fig. 4) were found :1 (pH = 4.5-6.5), 2 (pH = 6.5-9) and 3 (pH = 8.5-10). Various voltammetric results indicated that these reduction processes correspond to following species:
1) FeL and FeL_2^{3-} complexes, where malic acid is considered as three-protons acid (H_3L).
2) $Fe(mal)_2(OH)_x$
3) $Fe(mal)_2(OH)_y$ with y > x.
Time dependence of the reduction process showed that these complexes are present in solution for several months (1), .or weeks (2 and 3).
The UV-Vis spectra (Fig. 5) analysis indicated the presence of two spectrally distinguishable Fe(III)-malate species: presumably FeL and FeL_2^{3-} complexes (1). At pH > 6.5 spectra remained almost unchanged, therefore, Fe(III)-malate complexes 2 and 3 weren't detected by UV-Vis spectrophotometry because chemical changes which led to their formation (intramolecular bond cleavage and binding of OH^- ions) were unlikely to be registered by this technique.

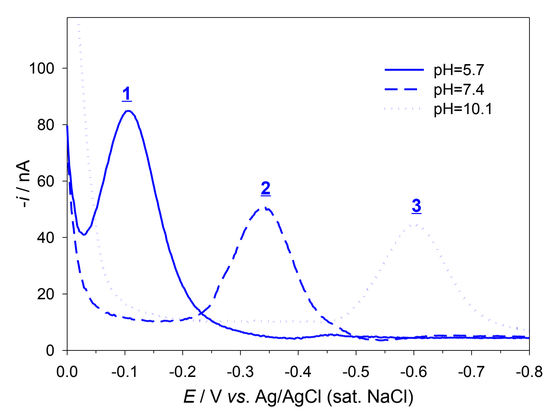

Figure 4. Voltamograms of Fe(III)-malate complexes at different pH. c_{Fe}= 4x10^{-5} mol dm^{-3}, c_{mal} = 0.1 mol dm^{-3}.

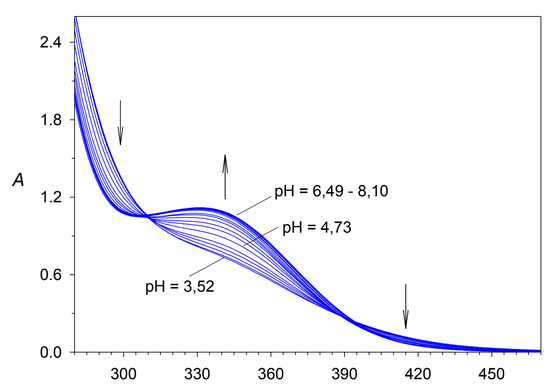

Figure 5. UV-Vis spectra of Fe(III)-malate complexes recorded as function of pH. l = 10 cm, c_{mal} = 0.1 mol dm^{-3}, c_{Fe} = 4x10^{-5} mol dm^{-3}.

III. Fe(III)-citrate complexes

Four different reduction processes (Fig. 6 A and B) of iron(III)-citrate complexes were detected in the pH range from 4 to 9, depending particularly on the c_{cit}:c_{Fe} ratio.
Voltammetric investigations indicated following species reduction processes:
1) $Fe(cit)(OH)_x$
2) FeL_2^{5-}, FeL_2H^{4-} and $FeL_2H_2^{3-}$, where citric acid is considered as four-proton acid (H_4L)
3) $Fe_x(cit)_y$ (x ≥ 2), e.g. polynucelar complex
4) $Fe(cit)_2(OH)_x$
The analysis of UV-Vis spectra given in Fig.7 A, indicated existence of 1:1 and 1:2 Fe(III):citrate complexes, which was in agreement with voltammetric results (1 and 2). The analysis of spectra in Fig. 7 B pointed out presence of the same species as determined in voltammetric measurements (2).

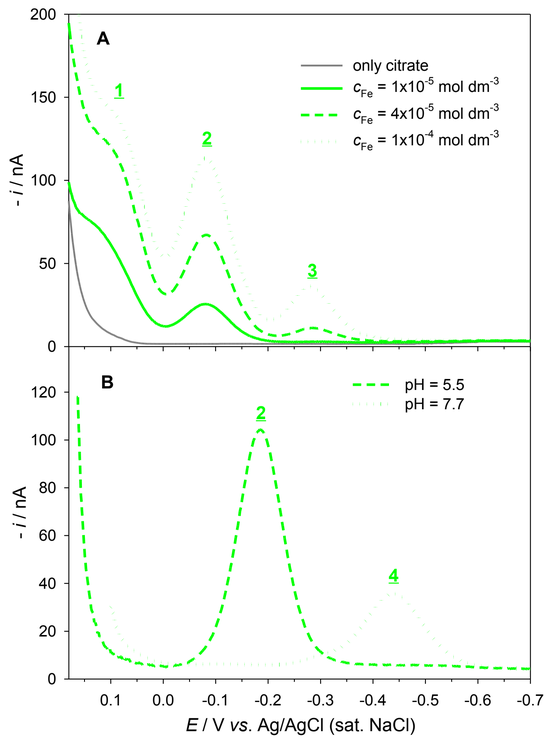

Figure 6. Voltamograms of Fe(III)-citrate complexes as function of: A) c_{Fe} (c_{cit}= 10^{-3} mol dm^{-3}, pH = 5.5) B) pH (c_{Fe}= 4x10^{-5} mol dm^{-3}, c_{cit}= 0.1 mol dm^{-3}).

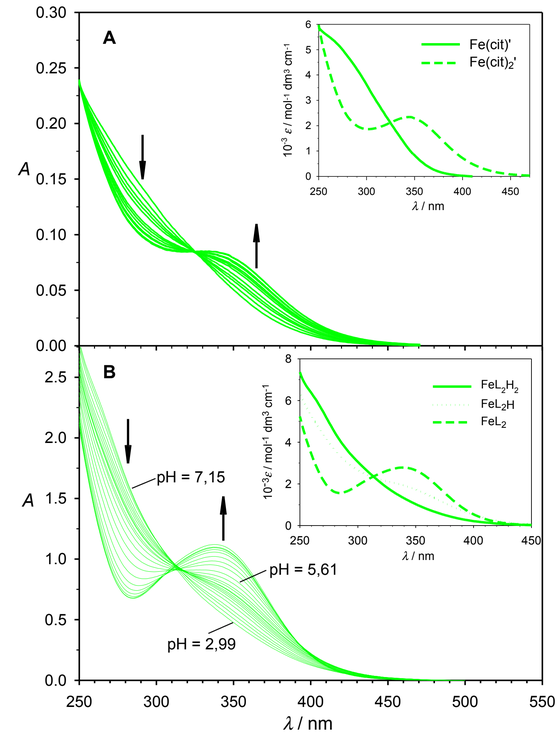

Figure 7. UV-Vis spectra of Fe(III)-citrate complexes recorded as function of: A) c_{cit} (pH = 5.5, c_{cit} =(1-10)x10^{-3} mol dm^{-3}, c_{Fe}= 4x10^{-5} mol dm^{-3}), B) pH (c_{cit} =(0.1 mol dm^{-3}, c_{Fe}= 4x10^{-4} mol dm^{-3}). l = 1 cm. Insets: calculated electronic spectra.

Conclusion

Results showed that organic acids, citric, malic and succinic, form stable complexes with Fe^{3+} in the pH range from 4 to 10 in model solutions, as well as in the seawater. However, due to differences in their structures: succinc and malic acid in one –OH group; malic and citric in $–CH_2COOH$ group, that acids as ligands gave significantly different complexes with a Fe^{3+} ion, considering their structure and chemical characteristics. –OH group of malic and citric acid participate in the coordination of Fe^{3+} ion that results in greater stability of Fe(III)-malate and Fe(III)-citrate complexes in comparison to Fe(III)-succinate complexes.
Since complexes are dissolved in the solutions for rather long period of time, it can be presumed that they would be bioavailable to organisms in the seawater and, therefore, could be used in Fe-enrichment experiments in HNLC areas of oceans.

References

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[2] S. H. Brunner, *The role of iron in present day biogeochemistry cycling (review)*, Term Paper, ETH, Zurich, 2007.
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[4] J. H. Martin, R. M. Gordon, S. E. Fitzwater, *Nature* **345** (1990) 156-158.